



CASE TW/4-22810/A/PCT

1755 AF

CERTIFICATE OF MAILING

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Deborah A. Pinori
Type or print name

Deborah A. Pinori
Signature

August 21, 2008
Date

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF
JEAN-JACQUES DONZÉ ET AL
APPLICATION NO: 10/537,062
FILED: JUNE 1, 2005
FOR: MIXTURES OF FLUORESCENT WHITENING
AGENTS

Group Art Unit: 1755
Examiner:

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

TRANSMITTAL LETTER

Sir:

Enclosed herewith are three copies of the Appeal Brief in the above-identified application.

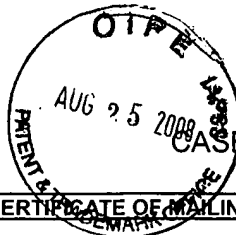
- ☒ Please charge Deposit Account No. 03-1935 in the amount of \$500.00 for payment of the fee. Two additional copies of this paper are here enclosed. The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment, to Account No. 03-1935.
- ☒ Enclosed is a Petition for Extension of time.

Respectfully submitted,

Shiela A. Loggins

Shiela A. Loggins
Agent for Applicants
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540 White Plains Road
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8/21/2008



CASE TW/4-22810/A/PCT

CERTIFICATE OF MAILING

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Deborah A. Pinori
Type or print name

Deborah A. Pinori
Signature

8/21/08
Date

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE PCT NATIONAL STAGE APPLICATION OF
JEAN-JACQUES DONZÉ ET AL
INTERNATIONAL APPLICATION NO. PCT/EP 03/50913
FILED: DECEMBER 1, 2003
FOR: MIXTURES OF FLUORESCENT
WHITENING AGENTS
U.S. APPLICATION NO: 10/537,062
35 USC 371 DATE: JUNE 1, 2005

Group Art Unit: 1755
Examiner: John A. Hevey

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

APPEAL BRIEF

Sir:

This appeal is from the final rejection mailed from the PTO on February 22, 2008.

A Notice of Appeal was mailed on May 21, 2008 .

Mailing of this Appeal Brief is timely and accompanied by the requisite fee under 41.20 and a petition for a one (1) month extension of time.

The Commissioner is authorized to charge any fee due, or credit any overcharge, as a result of this Amendment to Deposit Account No. 03-1935.

(1) REAL PARTY OF INTEREST

The real party of interest, by virtue of an assignment recorded in the United States Patent and Trademark Office on December 19, 2005 reel/frame 017363/0020 is:

Ciba Specialty Chemicals Corporation (now Ciba Corp.)
P.O. Box 2005
540 White Plains Road
Tarrytown, New York 10591

(2) RELATED APPEALS AND INTERFERENCES

Appellant is not aware of any related appeals and interferences for the above application.

(3) STATUS OF THE CLAIMS

Claims 2, 10-11 are cancelled. Claims 1, 3-9 and 12-16 are pending. Claims 1, 3-9 and 12-16 are rejected.

Claims 1, 3-9 and 12-16 are being appealed.

Claims 1 and 7 are being argued separately.

(4) STATUS OF AMENDMENTS

The claims now stand on Appeal as amended on November 27, 2007.

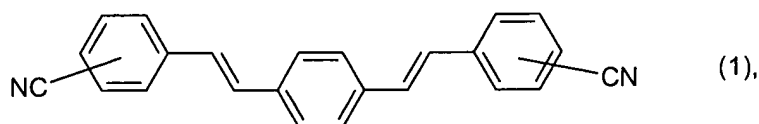
This brings up to date the status of the claims. A clean copy of the claims is attached in the (8) Claims Appendix.

(5) SUMMARY OF THE CLAIMED SUBJECT MATTER

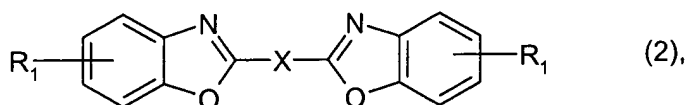
Claim 1 is the only independent claim. However, as appellants will argue both claim 1 and claim 7 separately, appellants submit a summary of claims 1 and 7 below:

Claim 1

Claim 1 is directed to a mixture of fluorescent whitening agents comprising 13 to 17 % by weight of a compound of formula (1)

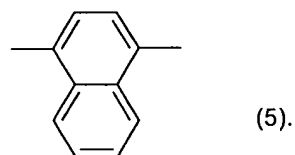
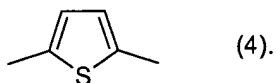
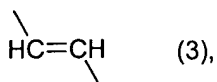


and 83 to 87 % by weight of one or more compounds of formula



wherein R₁ denotes hydrogen, C₁-C₆alkyl, C₅-C₁₄aryl or C₆-C₂₄aralkyl and

X is a bivalent radical of formula (3), (4) or (5)



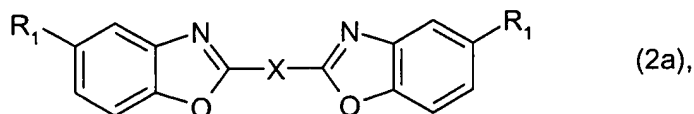
Support for the above claim may be found on page 1, lines 16 to the bottom of the page through page 2, line 5.

Further support for the combinations of formula (1) and (2) within the narrow weight % ranges may be found in the examples on pages 5-7.

Claim 7

Claim 7 depends from claim 4 which ultimately depends from claim 1.

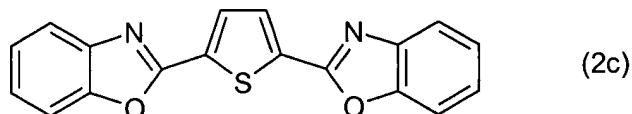
Claim 4 is directed to a mixture according to claim 1 comprising a compound of formula (2a)



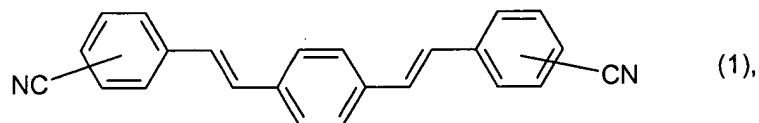
wherein R₁ and X are as defined in claim 1.

Claim 7 is directed to a mixture according to claim 4 comprising a compound of formula (2a) wherein R₁ denotes hydrogen and X is a bivalent radical of formula (4). Thus Claim 7 is directed to a mixture of

a formula designated (2c) in the specification on page 3 of the specification



and formula (1) of claim 1



This combination is well supported in the examples on pages 5-7.

The mixtures of claim 1 and claim 7 provide a blue shade without the addition of shading dyes.

Furthermore, the materials treated with the mixtures according to the invention exhibit a high lightfastness as well as a high whiteness level and excellent brilliancy. Support for these stated advantages can be found on page 5, lines 1-4.

(6) GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

Claims 1, 3-9 and 12-16 are rejected under 35 USC 103(a) as being unpatentable over Fringeli et al., US5053055.

(7) ARGUMENTS

Claim 1 and claim 7 are argued separately under separate headings.

Claim 1

The instant case claims a mixture of whitening agents comprising 13 to 17 wt. % a distyrylbenzene and 83-87 wt. % of a bis-benzoxazole.

Examiner believes Fringeli to teach a compound or mixture of fluorescent whitening agents selected from a group containing di-styrylbenzenes, bis-benzoxazoles, bis-benzoxasoles-thiophenes, bis-benzoxazoles-naphthalenes, stilbenes, etc.

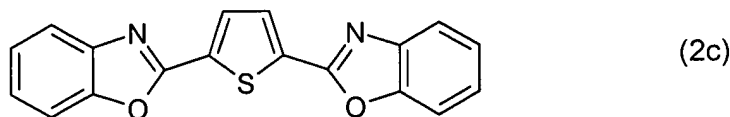
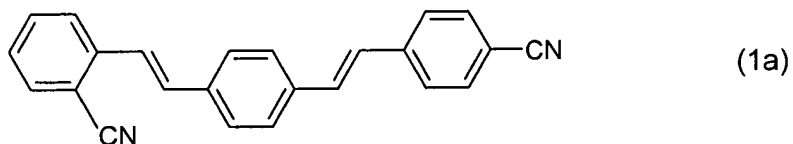
Fringeli further teaches mixtures comprising 60-85 wt. % of a bis-benzoxazoles (mixture IV and VI column 9) and separately mixtures comprising 13-80 wt. % specific di-styrylbenzene compounds (mixtures I-III, and V, columns 8 and 9).

Fringeli fails to teach a specific example of a mixture having both fluorescent whitening agents as required by claim 1 which is within the wt. ranges of 83-87 wt. % for the bis-benzoxazole and 13-17 wt. % of the di-styrylbenzene presently claimed.

The examiner further states on page 4, item 4c) of his February 22, 2008 Office Reply that it would have been obvious to one of ordinary skill in the art to substitute the use of alternative whitening agents to arrive at the same fluorescent whitening material as required by instant claims because Fringeli suggests the use of 60-85% of a compound of Formula 2 (e.g. mixtures IV and VI, col. 9) and 15-40 % of an additional brightener with a compound of Formula 1, as essential components to make various fluorescent whitening products.

The appellant is aware that when seeking to overcome a prima facie case of obviousness by showing improved performance in a range that is within or overlaps with a range disclosed in the prior art, the appellant must show that the claimed range is critical, generally by showing that the claimed range achieves unexpected results relative to the prior art range.

In order to rebut a prima facie case of obviousness, the appellants have submitted two declarations which have been considered by the examiner. The submitted declarations which have compared mixtures of fluorescent whitening agents of formula 1a and 2c at various wt %.



The Second Declaration submitted on April 16, 2008 and entered by the examiner in his advisory action of May 14, 2008 contains the same data as the earlier declaration but includes an additional data point and a detailed explanation of the standard deviation for the tint value. Further, the expert, Jean-Jacques Donze, explains the significance of the resulting differences in light fastness values and tint values for each of the three examples.

Fingeli suggests ranges from 60-85% of a compound of Formula 2 (e.g. mixtures IV and VI, col. 9) and 15-40 % of an additional brightener with a compound of Formula 1.

Although not cited in the examiner's rejection, US 4,778,623 exemplifies (example 22, col. 24-25) a specific fluorescent whitening mixture of compounds of formula 1a and 2c. See above. The weight ratios of the specific mixture in example 22 of US '623 is 1:2 or 33 wt.% compound of formula 1a and 67 wt. % compound of formula 2c. This reference is also included in the Evidence Appendix (9).

The appellants believe this reference, US 4,778,623, to be the closest prior art in that US 4,778,623 actually exemplifies mixtures of fluorescent whitening agents which are encompassed by formula (1) and (2) as presently claimed. Examiner agrees that Fingeli fails to teach a specific example of the mixture of fluorescent whitening agents. Not only, does US '623 exemplify mixtures of compounds of formula (1) and (2) but also suggests mixtures in the weight ranges overlapping with the presently claimed weight ranges. In col. 11 lines 53 and 56 mixtures of compounds encompassed by formula (1) at 5-90 wt. % and compounds of formula (2) at 95-10 wt. % are taught.

Thus appellants have used the example 22 of US 4,778,623 for its direct comparison in the submitted declarations. The appellants believe this comparison is justified and the proper one.

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This justification resides in the fact that example 22 of US 4,778,623 teaches specific examples of compounds encompassed by formulae (1) and (2) and by analogy also work as a comparison to show unobviousness in the overlapping ranges taught by Fingeli (60-85% of a compound of formula 2 and 15-40% of a compound of formula (1)). Thus the comparison drawn by the Appellants, although not directly drawn from Fingeli as Fingeli teaches no specific examples of mixtures of formula (1) and (2), is the proper comparison.

Appellants have compared their system with the most relevant prior art. It is not required that the claimed invention be compared with subject matter that does not exist in the prior art. Fingeli, as agreed by the examiner makes no specific example of a mixture having both fluorescent whitening agents (Formula 1 and 2). US 4,778,623 exemplifies a mixture of fluorescent whiteners of formula (1) and (2). The appellant is not required to create prior art but has instead compared with the closest art actually taught and by analogy has also shown the present claim 1 to be unobvious in light of Fingeli.

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Thus the First and Second Declarations of record involves a very close comparison wherein the closest prior art, 33 wt. % of 1a and 67 wt. % of 2c (example 22 of US 4,778,623) is compared with the closest possible claimed mixture of compounds 1a and 2c at wt. % within the very narrowly presently claimed wt. ranges.

The examiner has stated that although the affidavit may demonstrate slight differences over claimed closest prior art, it does not display unexpected, unobvious, or superior results. While certain test values of the instant application such as tint value may be slightly superior in the art, the whiteness value for example is slightly inferior. See Advisory Action of May 14, 2008.

Examiner further alleges the submitted 132 affidavit evidence is not commensurate with the scope of the claims. Only one comparison example is given which selects the highest end of the range of formula 1 and lowest end of formula 2 and does not show a representative range of the instant invention versus the prior art.

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The appellants submitted the Second Declaration as explained above which added an additional comparison point. The appellants submit that the Second Declaration shows unobvious advantages when the mixtures of compound of formula (1) and compound of formula (2) are combined in a very narrow wt. % range and thus rebuts the examiner's case of prima facie obviousness. Furthermore, appellants believe the showing to be commensurate in scope with the present claim 1.

The Second Declaration Shows Unobvious Results

Table 1:

Example	Mixture of FWA	Amount	Ganz Whiteness	Tint Value	Light Fastness
A ^{a)}	33 % (1a) 67 % (2c)	0.12 %	215	2.2	6-7
B ^{b)}	17 % (1a) 83 % (2c)	0.12 %	213	1.9	7
C ^{b)}	15% (1a) 85% (2c)	0.12 %	212	1.9	7

- a) Comparison Example according to U.S. 4,778,623 (Examples 20/22).
b) Example according to the invention.

The above results have been discounted by the examiner. To reiterate, the examiner states that the affidavit may demonstrate slight differences over claimed closest prior art, it does not display unexpected, unobvious, or superior results. While certain test values of the instant application such as tint value may be slightly superior in the art, the whiteness value for example is slightly inferior.

It is well settled that superior properties need not be shown in every environment. Evidence that a compound is unexpectedly superior in one of a spectrum of common properties, as here, can be enough to rebut a prima facie case of obviousness. The appellants respectfully point out that the inventive mixtures are considerably more light stable than mixtures disclosed in the closest prior art and by analogy the cited prior art, Fingeli.

As explained in the second Declaration,

In terms of lightfastness, a rating of 6 corresponds to a significant fading after 220 hours exposure in the Xenotest and 90 days exposure to daylight in Basle, CH. A rating of 7 corresponds to 400 hours in the Xenotest and 170 days exposure to daylight in Basle, CH. Thus a 6-7 rating corresponds to about 310 hours Xenotest and 130 days exposure to daylight in Basle, CH which is clearly considerably worse than a rating of 7. All textile finishers consider the difference between 6-7 and 7 as meaningful and significant.

The appellants believe the PTO has not provided any persuasive basis to question this comparative data and assertion that the demonstrated results were unexpected.

In regard to the examiners statement that the showing is not commensurate with the scope of the claims, the appellants point out that the scope of the claims is very narrow.

Formula (1) encompasses only isomers of cyano substituted bis styrylbenzenes at 13 to 17 wt. %.

Formula (2) encompasses three types of bis-benzoxaxoles-bis-benzoxaxolyl-ethylenes, bis-benzoxazolyl-thiophens and naphtyl linked bezoxazolyls at 83 to 87 wt. %.

It is well established that comparisons need only be to compounds which are actually taught, not to compounds not exemplified. US 4,778,623 only exemplifies compounds of formula (1a) and (2c). Thus Appellants have met their burden of evidence as to the exact compounds compared.

In regard to the weight % compared, appellants have submitted two data points.

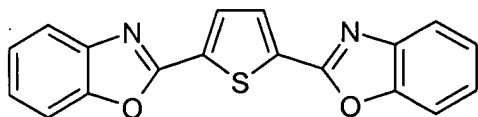
Example B 17% (1a) and 83% (2c)

Example C 15% (1a) and 85% (2c)

These inventive examples (B and C) are compared to ranges in the prior art which are actually taught and the inventive examples are shown to be considerably more light stable. The Appellant has clearly established a surprising advantage at the highest end of the range of formula 1 and lowest end of formula 2. Furthermore, Example C shows that as one moves to the middle of the weight range for formula 1 and the middle of the weight range for formula 2, the same advantages are retained (higher light stability) indicating a trend. Thus the appellants have made a showing which is reasonably commensurate in scope with the claim limitations and no more should be required.

Claim 7

Claim 7 is directed to a formula (2a) which is:



This compound is identical to the bis-benzoxazole (2c) used in the First and Second Declaration.

As stated above the examiner has discounted appellants affidavits and does not believe that they show unexpected results. The appellants have shown above that this statement by the examiner is clearly erroneous. One skilled in the art would not expect mixtures of fluorescent whitening agent of formula (1) and (2) to give more highly light stable compositions when the weight % of the compounds of the mixtures are varied within a very narrow claimed range.

This evidence is particularly clear in regard to the compound represented by claim 7 as this is the compound used to make the showing (2c).

The statement by the examiner that the showing is not commensurate with the scope of the claim is particularly unreasonable in regard to claim 7. The showing represents the actual compounds claimed and the compounds actually taught in the prior. The weight ranges tested show a trend of higher light stability within the narrow weight ranges claimed when compared to the actually taught prior art.

In light of the above discussions, Appellants respectfully submit that the rejections of claims 1 and 7 have been rebutted and respectfully ask that the rejections be reconsidered and reversed.

Respectfully submitted,



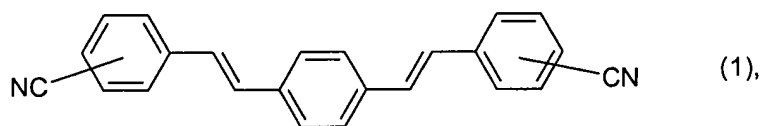
Shiela A. Loggins
Agent for Appellants
Reg. No. 56,221
filed under 37 CFR 1.34(a)

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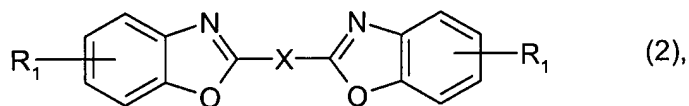
Enclosures: Fee letter, Petition for one (1) month extension of time, (8) Claims Appendix with clean copy of the claims on appeal, (9) Evidence Appendix which includes a First Declaration and Second Declaration and US 4,778,623 and (10) Related Proceedings Appendix

(8) CLAIMS APPENDIX

1. (previously presented): A mixture of fluorescent whitening agents comprising 13 to 17 % by weight of a compound of formula

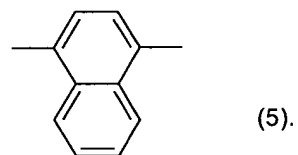
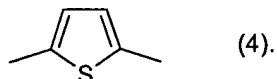
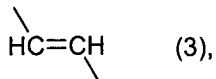


and 83 to 87 % by weight of one or more compounds of formula



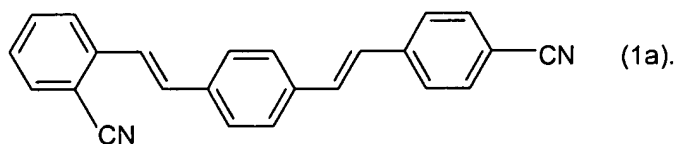
wherein R_1 denotes hydrogen, C_1 - C_6 alkyl, C_5 - C_{14} aryl or C_6 - C_{24} aralkyl and

X is a bivalent radical of formula (3), (4) or (5)

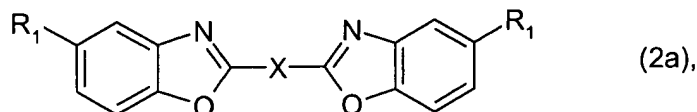


2. (cancelled).

3. (previously presented): A mixture according to claim 1 comprising a compound of formula (1a)



4. (previously presented): A mixture according to claim 1 comprising a compound of formula (2a)



wherein R₁ and X are as defined in claim 1.

5. (original): A mixture according to claim 4 comprising a compound of formula (2a) wherein R₁ denotes hydrogen or C₁-C₆alkyl.

6. (original): A mixture according to claim 4 comprising a compound of formula (2a) wherein R₁ denotes methyl and X is a bivalent radical of formula (3).

7. (original): A mixture according to claim 4 comprising a compound of formula (2a) wherein R₁ denotes hydrogen and X is a bivalent radical of formula (4).

8. (previously presented): A composition, which contains water, a mixture of fluorescent whitening agents according to claim 1 and, optionally, auxiliaries.

9. (previously presented): A composition according to claim 8 containing water and, based on the total weight of the formulation, from 3 to 25% by weight of the fluorescent whitening agent mixture and 0 to 60% of auxiliaries.

10-11. (cancelled).

12. (previously presented): A composition according to claim 9 containing water and, based on the total weight of the formulation, from 10 to 20% by weight of the fluorescent whitening agent mixture and 5 to 50% by weight of auxiliaries.

13. (previously presented): A method of whitening synthetic fibres, which comprises contacting said fibres in an aqueous medium with a fluorescent whitening agent mixture according to claim 1.

14. (previously presented): A method of whitening synthetic fibres, which comprises contacting said fibres in an aqueous medium with a fluorescent whitening agent composition according to claim 8.

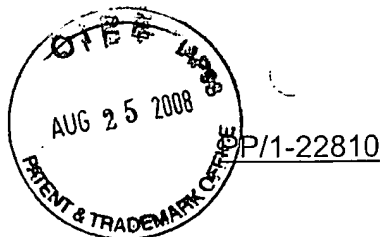
15. (previously presented): A method according to claim 13, wherein the synthetic fibres comprise polyester fibres.

16. (previously presented): A method of whitening synthetic fibres, which comprises contacting said fibres in an aqueous medium with a fluorescent whitening agent mixture according to claim 3.

(9) EVIDENCE APPENDIX

Appellants submitted two Declarations under 132 both signed by Jean-Jacques Donze and mailed on April 24, 2007 to the USPTO. The First Declaration was mailed on November 27, 2007 after the first office action and the Second Declaration was mailed on April 16, 2008 and entered by the examiner in his advisory action of May 14, 2008.

Also included in this Evidence Appendix is US 4,778,623.



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF
JEAN-JACQUES DONZÉ ET AL.

SERIAL NO. 10/537,062

FILED: JUNE 1, 2005

FOR: Mixtures of Fluorescent Whitening Agents

Group Art Unit: 1709

Examiner: HEVEY, JOHN A.

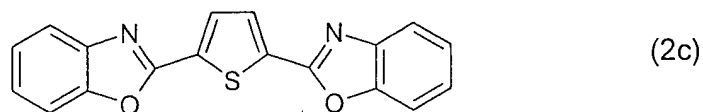
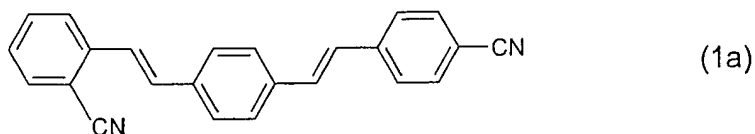
Commissioner of Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

DECLARATION UNDER RULE 132

I, Jean-Jacques Donzé, a citizen of France, residing in F-68740 Blodelsheim, France, hereby declare:

1. That I have studied Chemistry at the Université de Haute-Alsace, Mulhouse, France, and have been awarded the degree of a Doctor in 1973.
2. That I have been employed at the Textile Research Center in Mulhouse from 1975 to 1987.
3. That I have been employed by Ciba-Geigy AG Basel, Switzerland, in January 1988, later Ciba Specialty Chemicals Inc. and Huntsman, as Chemist in the marketing of textile effects and since June 2007 in Research and Application Technology of textile effects at Huntsman.
4. That I have been engaged in application technology of fluorescent whitening agents.
5. That I am a co-inventor of U.S. Patent Application Serial No. 10/537,062 to Jean-Jacques Donzé et al. and that I am familiar with the subject matter thereof.
5. That the experiments described in the following have been made under my supervision.

Tested Fluorescent Whitening Agents (FWA):



Testing Conditions:

A polyester fabric (prescoured, heat-set at 195°C, 165 g/m²) is treated in a dyeing apparatus at room temperature and at a liquor ratio of 1:20 with an aqueous bath containing a mixture of the fluorescent whitening agents of formula (1a) and (2c) in the ratios given in Table 1 and in the presence of 1 g/l of a fatty alcohol polyglycol ether as dispersing agent. The temperature is raised from room temperature to 130°C over 30 minutes, held for a further 30 minutes at this temperature and subsequently cooled to 40°C during 15 minutes. The textile material is then rinsed for 30 seconds under running water and dried at 70°C. The Ganz whiteness, tint value and light fastness (according to ISO 105- B02) is measured. The results are summarized in Table 1.

Table 1:

Example	Mixture of FWA	Amount	Ganz Whiteness	Tint Value	Light Fastness
A ^{a)}	33 % (1a) 67 % (2c)	0.12 %	215	2.2	6-7
B ^{b)}	17 % (1a) 83 % (2c)	0.12 %	213	1.9	7

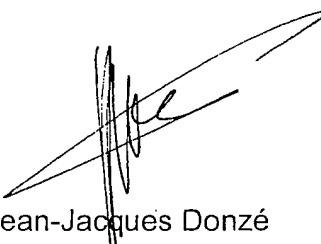
- a) Comparison Example according to U.S. 4,778,623 (Examples 20/22).
b) Example according to the invention.

Discussion of Results:

The obtained results show that Example B according to the invention clearly shows several advantages in comparison to the known Example A. The Ganz whiteness is very similar in Examples A and B. However, Example B shows a clearly less greenish effect with a tint value below 2.0. A greenish shade is seen as a clear disadvantage by textile finishers. Additionally, Example B according to the invention shows a clearly better light fastness. The results are surprising and could not be expected.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 1st day of November, 2007



Jean-Jacques Donzé

IN RE APPLICATION OF
JEAN-JACQUES DONZÉ ET AL.
SERIAL NO. 10/537,062
FILED: JUNE 1, 2005
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Group Art Unit: 1709
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Alexandria, Virginia 22313-1450

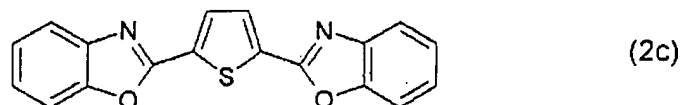
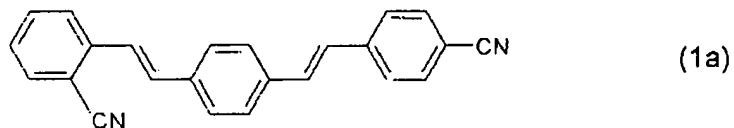
SECOND DECLARATION UNDER RULE 132

I, Jean-Jacques Donzé, a citizen of France, residing in F-68740 Blodelsheim, France, hereby declare:

1. That I have studied Chemistry at the Université de Haute-Alsace, Mulhouse, France, and have been awarded the degree of a Doctor in 1973.
2. That I have been employed at the Textile Research Center in Mulhouse from 1975 to 1987.
3. That I have been employed by Ciba-Geigy AG Basel, Switzerland, in January 1988, later Ciba Specialty Chemicals Inc. and Huntsman, as Chemist in the marketing of textile effects and since June 2007 in Research and Application Technology of textile effects at Huntsman.
4. That I have been engaged in application technology of fluorescent whitening agents.
5. That I am a co-inventor of U.S. Patent Application Serial No. 10/537,062 to Jean-Jacques Donzé et al. and that I am familiar with the subject matter thereof.
5. That the experiments described in the following have been made under my supervision.

J. 1975

Tested Fluorescent Whitening Agents (FWA):



Testing Conditions:

A polyester fabric (prescourd, heat-set at 195°C, 165 g/m²) is treated in a dyeing apparatus at room temperature and at a liquor ratio of 1:20 with an aqueous bath containing a mixture of the fluorescent whitening agents of formula (1a) and (2c) in the ratios given in Table 1 and in the presence of 1 g/l of a fatty alcohol polyglycol ether as dispersing agent. The temperature is raised from room temperature to 130°C over 30 minutes, held for a further 30 minutes at this temperature and subsequently cooled to 40°C during 15 minutes. The textile material is then rinsed for 30 seconds under running water and dried at 70°C. The Ganz whiteness, tint value and light fastness (according to ISO 105- B02) is measured. The results are summarized in Table 1.

Table 1:

Example	Mixture of FWA	Amount	Ganz Whiteness	Tint Value	Light Fastness
A ^{a)}	33 % (1a) 67 % (2c)	0.12 %	215	2.2	6-7
B ^{b)}	17 % (1a) 83 % (2c)	0.12 %	213	1.9	7
C ^{b)}	15% (1a) 85% (2c)	0.12 %	212	1.9	7

a) Comparison Example according to U.S. 4,778,623 (Examples 20/22).

b) Example according to the invention.

Discussion of Results:

The obtained results show that Examples B and C according to the invention clearly show several advantages in comparison to the known Example A. The Ganz whiteness is very similar in Examples A, B and C. However, Examples B and C show

a clearly less greenish effect with a tint value below 2.0. A greenish shade is seen as a clear disadvantage by textile finishers. Additionally, Examples B and C according to the invention show a clearly better light fastness. The results are surprising and could not be expected.

In terms of lightfastness, a rating of 6 corresponds to a significant fading after 220 hours exposure in the Xenotest and 90 days exposure to daylight in Basle, CH. A rating of 7 corresponds to 400 hours in the Xenotest and 170 days exposure to daylight in Basle, CH. Thus a 6-7 rating corresponds to about 310 hours Xenotest and 130 days exposure to daylight in Basle, CH which is clearly considerably worse than a rating of 7. All textile finishers consider the difference between 6-7 and 7 as meaningful and significant.

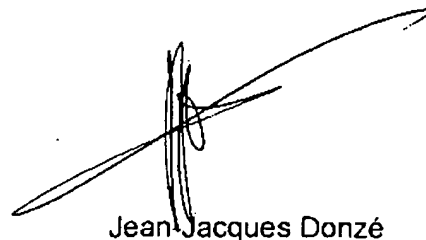
In terms of tint value for fluorescent white, the tolerance is by 0.2 difference. This tolerance is for example, specified by most brandhouses such as NIKE and Express. This tint value is an average of 4 measurements. One skilled in the art would say that the difference between 1.9 and 2.2 is known as significant when visually assessed. The whitened fabric sample with 2.2 appears really greener. It is known that such a greening is usually seen as a disadvantage by most textile finishers as being associated with a lack of development of the whitening agent.

The standard deviation for the tint value is about ± 0.05 .

There is no standard deviation for the light fastness value as a 7 verses a 6-7 value is without any tolerance or deviation due to the big difference in exposure time between the data.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this JSth day of April, 2008



Jean Jacques Donzé

United States Patent [19]
Guglielmetti

[11] **Patent Number:** 4,778,623
[45] **Date of Patent:** Oct. 18, 1988

- [54] **FLUORESCENT BRIGHTENERS
CONSISTING OF BIS-STYRYLBENZENE
COMPOUNDS, A PROCESS FOR THEIR
PREPARATION AND THEIR USE**
- [75] **Inventor:** Leonardo Guglielmetti, Bottmingen,
Switzerland
- [73] **Assignee:** Ciba-Geigy Corporation, Ardsley,
N.Y.
- [21] **Appl. No.:** 756,382
- [22] **Filed:** Jul. 18, 1985

Related U.S. Application Data

- [60] Division of Ser. No. 474,731, Mar. 18, 1983, which is a
continuation of Ser. No. 213,150, Dec. 4, 1980, aban-
doned.

[30] Foreign Application Priority Data

Dec. 13, 1979 [CH] Switzerland 11040/79
Apr. 21, 1980 [CH] Switzerland 3058/80

- [51] **Int. Cl.⁴** C09K 11/06; C07C 119/048
[52] **U.S. Cl.** 252/301.21; 252/301.22;
558/411
[58] **Field of Search** 252/301.21, 301.22,
252/301.23, 301.24, 301.25; 558/411

[56] References Cited

U.S. PATENT DOCUMENTS

4,330,427 5/1982 Martini et al. 252/301.24
4,336,155 6/1982 Martini et al. 252/301.21

FOREIGN PATENT DOCUMENTS

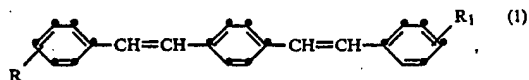
0023027 1/1981 European Pat. Off. .
0032254 7/1981 European Pat. Off. .
1045443 10/1966 United Kingdom .

Primary Examiner—John F. Niebling
Assistant Examiner—Steven P. Marquis

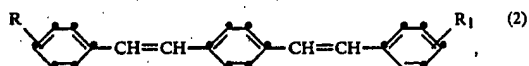
Attorney, Agent, or Firm—Wenderoth, Lind & Ponack

[57] ABSTRACT

A fluorescent brightener is proposed which consists of
51–99% of an unsymmetrically substituted compound
of the formula



in which R and R₁ are identical or different and, if R
and R₁ are identical, R₁ must occupy a position in the
phenyl ring to which it is bonded which differs from the
position occupied by R in its phenyl ring, and in which
R and R₁ independently of one another are CN or a
carboxylic acid ester group, and 49–1% of a symmetri-
cally substituted compound of the formula



in which R as defined above and the two R's are bonded
to identical positions in their phenyl rings, as are also
agents which contain these fluorescent brighteners and
the use of these fluorescent brighteners for the fluo-
rescent brightening of, in particular, textile materials, pre-
ferably made of polyester. The said fluorescent brighten-
ers are prepared by reacting terephthalaldehyde prefer-
ably with a correspondingly substituted benzylphos-
phonate and further reacting the resulting mixture of a
correspondingly substituted 4-stilbene aldehyde and a
symmetrical p-bis-styrylbenzene with a benzylphos-
phonate which differs from the benzylphosphonate first
used.

24 Claims, No Drawings

FLUORESCENT BRIGHTENERS CONSISTING OF BIS-STYRYLBENZENE COMPOUNDS, A PROCESS FOR THEIR PREPARATION AND THEIR USE

This application is a division of application Ser. No. 474,731, filed Mar. 18, 1983, which application is in turn a continuation of application Ser. No. 213,150, filed Dec. 4, 1980 (now abandoned).

The present invention relates to fluorescent brighteners consisting of two bis-styrylbenzene compounds, a process for their preparation and novel intermediates obtained in this process, agents containing fluorescent brighteners of this type and the use of these fluorescent brighteners and of the agents containing them for the fluorescent brightening of organic high molecular weight materials.

A large number of bis-styrylbenzene compounds and their use as fluorescent brighteners for diverse substrates has been disclosed in the literature. In this context see Swiss Patent Specification Nos. 366,512, 382,709, 388,294, 388,929, 389,585, 411,329, 416,078 and 465,548. Some of the individual components which are contained in the fluorescent brighteners of the composition according to the invention have been disclosed in the said publications, for example 1,4-bis-(2-, 3- or 4-cyanostyryl)-benzene or 1,4-bis-(4-methoxycarbonylstyryl)benzene. Some of these compounds are also available commercially. Furthermore, mixtures of 1,4-bis-styrylbenzene compounds have been disclosed which consist of three components, that is to say of about 50% of an asymmetrically substituted bis-styrylbenzene compound and about 25% of each of two different symmetrically substituted bis-styrylbenzene compounds. Such mixtures are formed purely statistically when one mol of terephthalaldehyde is reacted with a mixture of one mol of each of two substituted or unsubstituted benzylphosphates.

Mixtures of two or more symmetrically substituted bis-styrylbenzenes have also been disclosed which can be obtained by simple mixing of pure symmetrical compounds.

The use of the mixtures just described as fluorescent brighteners for diverse organic substrates, in particular of polyester, has also been disclosed. In this context see Swiss Patent Specification Nos. 366,512, 382,709, 416,078 and 465,548.

Further mixtures of three bis-styrylbenzene compounds have been disclosed in Swiss Patent Specification Nos. 366,512 and 382,709. Such mixtures are obtained by the simultaneous reaction of terephthalaldehyde with a mixture of 50-98 and especially 80-87% of a substituted benzylphosphonate and 50-2, and especially 20-3, % of a substituted benzylphosphonate which differs from the first substituted benzylphosphonate.

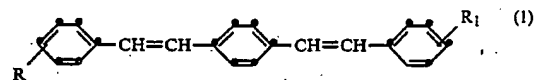
However, due to the process of preparation, these known three-component mixtures which have been mentioned can contain at most about 50% of the particular asymmetrically substituted bis-styrylbenzene compound.

It has now been found, surprisingly, that a fluorescent brightener consisting of 51-99%, preferably 80-99% and in particular 90-99% of an asymmetrically substituted 1,4-bis-styrylbenzene compound and 49-1%, preferably 20-1% and in particular 10-1% of a symmetrically substituted 1,4-bis-styrylbenzene compound is

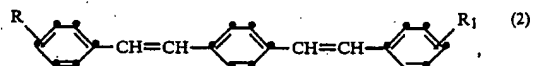
capable of producing considerably better white effects than the known corresponding individual compounds and the abovementioned mixtures.

Moreover, the fluorescent brightener of this composition can be prepared very well by the novel process according to the invention.

The fluorescent brightener according to the invention consists of 51-99% of an unsymmetrically substituted compound of the formula



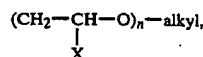
in which R and R₁ are identical or different and, if R and R₁ are identical, R₁ must occupy a position in the phenyl ring to which it is bonded which differs from the position occupied by R in its phenyl ring, and in which R and R₁ independently of one another are CN or a carboxylic acid ester group, and 49-1% of a symmetrically substituted compound of the formula



in which R is as defined above and the two R's are bonded to identical positions in their phenyl rings.

Thus, in every case the bis-styrylbenzene compound (1) must be unsymmetrically substituted. Preferably, the substituents R and R₁, irrespective of whether they are identical or different, are bonded to different positions of the particular phenyl rings. Compound (2) is symmetrical both in respect of the substituent R and in respect of its position.

Preferred carboxylic acid ester groups are those of the formula —COOY, in which Y is alkyl having 1 to 6 carbon atoms, alkenyl having 3 to 6 carbon atoms, cycloalkyl having 5 to 6 carbon atoms, halogenoalkyl, aralkyl, especially phenylalkyl, in particular benzyl, carbalkoxyalkyl, cyanoalkyl, hydroxyalkyl, aminoalkyl, alkylaminoalkyl or dialkylaminoalkyl, and all of the abovementioned combined alkyl groups in each alkyl moiety can have 1 to 6 carbon atoms; or Y is propargyl, tetrahydrofurfuryl or a group of the formula



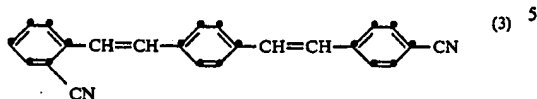
and in the lastmentioned group X is hydrogen or methyl and n is an integer between 1 and 4 and the alkyl group has 1 to 6 carbon atoms. Halogen is to be understood as meaning chlorine, bromine and fluorine, especially chlorine or bromine. The halogenoalkyl and hydroxyalkyl substituents can contain one or more halogen atoms or one or more hydroxyl groups.

Particularly preferentially, Y is alkyl having 1 to 6, and especially 1 to 4, carbon atoms, alkenyl having 3 to 6 carbon atoms and benzyl, in particular alkyl having 1 to 4 carbon atoms. All of the alkyl groups which belong to combined groups (which form the substituent Y) preferably have 1 to 4 carbon atoms.

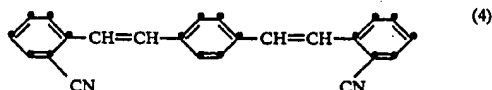
Fluorescent brighteners according to the invention in which R and R₁ in the individual components are identical and are each CN have particularly good properties.

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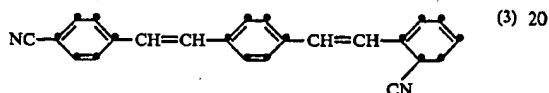
Fluorescent brighteners of particular interest in practice are the two fluorescent brighteners consisting of 51-99% of the compound of the formula



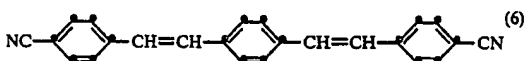
and 49-1% of the compound of the formula



and of 51-99% of the compound of the formula



and 49-1% of the compound of the formula



The fluorescent brighteners according to the invention have particularly valuable properties when they consist of 70-99, especially 80-99 but in particular 90-99% of the unsymmetrically substituted compound, for example of the formula (1) or (3), and 30-1, especially 20-1 but in particular 10-1% of the symmetrically substituted compound, for example of the formula (2), (4) or (6).

Particularly preferred compounds are, therefore, the fluorescent brightener consisting of 90-99% of the compound of the formula (3) and 10-1% of the compound of the formula (4) and the fluorescent brightener consisting of 90-99% of the compound of the formula (3) and 10-1% of the compound of the formula (6).

All of the percentages in this application are by weight, unless indicated otherwise.

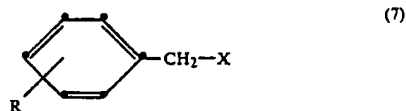
The fluorescent brighteners according to the invention are prepared by a novel process, which is likewise a subject of the invention.

When discussing the known bis-styrylbenzenes and the known mixtures thereof, the processes which result in such mixtures (statistical mixtures of 3 components) have also already been discussed. Furthermore, German Offenlegungsschrift No. 2,647,179 has disclosed how 2'-cyanostilbene-4-aldehyde, which occurs as an intermediate in the process according to the invention, can be obtained in the pure form with the aid of a multi-stage synthesis. See page 25, final paragraph to page 27, first paragraph of this publication: preparation of starting compound (3).

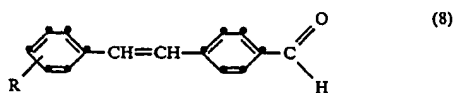
It has been found, surprisingly, that the fluorescent brighteners according to the invention can be prepared from two individual components by a very simple synthesis process.

The process according to the invention comprises reacting terephthalaldehyde with a compound of the formula

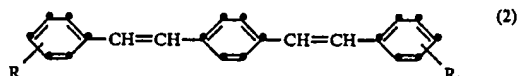
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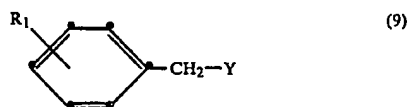
to give a mixture of the compounds of the formulae



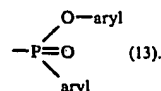
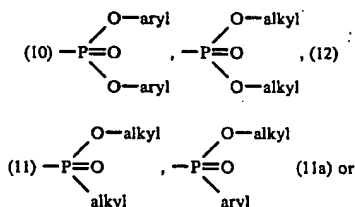
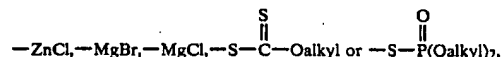
and



and then further reacting this mixture with a compound of the formula



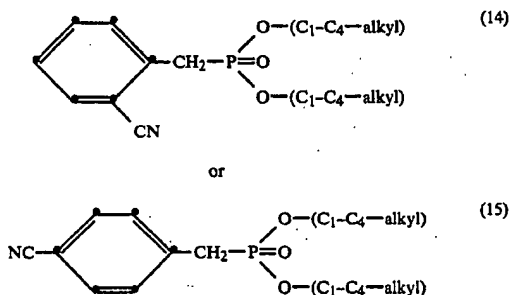
to give the fluorescent brightener consisting of the compounds (1) and (2), wherein R and R₁ are as defined in formulae (1) and (2) and have to satisfy the conditions given under these formulae with regard to their positions in the phenyl rings, and X and Y are identical or different and independently of one another are hydrogen or a radical of the formula -COOZ, in which Z is alkyl; or are radicals of the formulae -ZnBr,



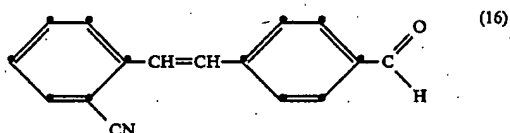
The ratio of terephthalaldehyde to the compound of the formula (7) is dependent on the ratio of unsymmetrically and symmetrically substituted bis-styrylbenzenes which is desired in the final mixture. Accordingly, the ratio of the monoaldehyde (8) to the compound of the formula (9) which reacts therewith can be adjusted to a suitable value. In this way, it is possible, by the choice of the ratios in the starting materials, easily to adjust the ratio to any of the ratios defined in claim 1. The monoaldehyde (8) content in the reaction mixture can be determined easily by analysis.

Preferably, the reaction is carried out with compounds of the formulae (7) and (9) in which X and Y in each case are a group of the formulae (10) to (13), and in particular a group of the formula (12). In the formulae (10) to (13), alkyl is preferably an unsubstituted alkyl group having 1 to 6 C atoms or the benzyl group, and aryl is preferably phenyl, which is unsubstituted or substituted by chlorine, methyl or methoxy.

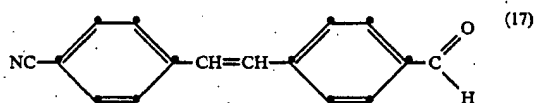
A preferred reaction within the scope of the process according to the invention, comprises reacting terephthalaldehyde with a compound of the formula



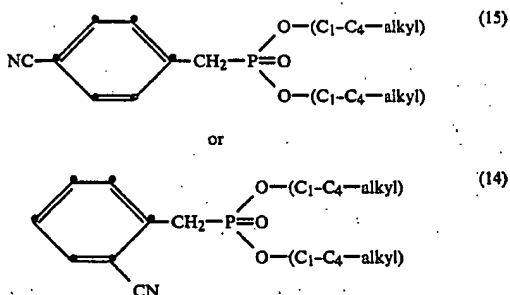
to give a mixture of the compounds of the formula



and of the formula (4) or to give a mixture of the compounds of the formula



and of the formula (6) and then reacting the particular mixture obtained with a compound of the formula



to give the fluorescent brighteners, according to the invention, consisting of the compounds of the formulae (3) and (4), or (3) and (6).

The reaction of terephthalaldehyde with a compound of the formula (7) in which X is one of the groups (10)-(13) or with a compound of the formula (14) or (15) (first stage) is preferably carried out in the presence of an alkaline condensing agent which serves as a proton acceptor. Suitable condensing agents of this type

are inorganic or organic bases, for example hydroxides, hydrides, alkoxides and amides of the alkali metals or alkaline earth metals, monomeric or polymeric strongly basic amines and exchange resins of the OH series. Sodium hydroxide, potassium hydroxide and sodium methylate are of particular importance in practice. A mixture of different bases can also be used. The amount of condensing agent to be used varies within wide limits. Advantageously, the equivalent amount is used, but it is also possible to use an excess. The second stage also (reaction of the mixture of monoaldehyde and symmetrical bis-styrylbenzene compound) is preferably carried out in the presence of the same condensing agent as described for the first stage.

The process according to the invention is advantageously carried out in a solvent which is inert under the reaction conditions. Such solvents are apolar and dipolar aprotic and protic solvents, for example hexane, octane, cyclohexane, toluene, xylene, chlorobenzene and the like; formamide, dimethylformamide, N-methylpyrrolidone, acetonitrile, dimethylsulfoxide and the like; and methanol, ethanol, isopropanol, hexanol and the like. The process according to the invention can also be carried out in water or in water-containing mixtures in the presence or in the absence of phase transfer catalysts.

The first stage is preferably carried out in a solvent in which the monoaldehydes of the formulae (8) or (16) and (17), which are formed, have low solubility, for example in methanol, ethanol, hexane or toluene. During the reaction, the aldehydes formed precipitate out together with the symmetrical compounds of the formulae (2) or (4) and (6) and can be isolated by filtration or, preferably, can be further reacted without isolation. If the resulting mixtures are isolated, they are then preferably employed in the subsequent stage without purification.

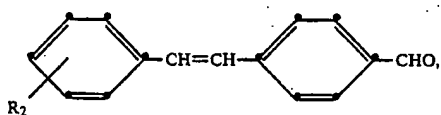
The reaction of the monoaldehydes of the formulae (8) or (16) and (17), as mixtures together with the symmetrical compounds of the formulae (2) or (4) and (6), with a compound of the formulae (9) or (15) or (14) (second stage) is preferably carried out in a solvent in which the monoaldehydes are partially or completely soluble. Such solvents are aprotic dipolar solvents, for example dimethylformamide, diethylformamide and dimethylsulfoxide.

The reaction temperature varies within wide limits, depending on the solvent chosen, and can be determined easily by preliminary experiments. The first stage is advantageously carried out at temperatures between 0° C. and 50° C., preferably at between 20° C. and 30° C. Suitable temperatures for the second stage are, in particular, temperatures of between 20° C. and 100° C. and preferably of between 30° C. and 50° C.

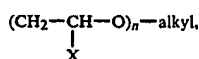
The compounds of the formulae (7) and (9) which are used as starting materials are known or can be prepared analogously to known processes (cf., for example, German Offenlegungsschrift No. 1,921,466 and British Patent Specification Nos. 920,988 and 929,436) or in accordance with Example 14 given below (preparation of the starting material).

The invention also relates to the novel compounds of the formulae (17) and (302), which occur as intermediates, specifically 4'-cyanostilbene-4-aldehyde and 3'-cyanostilbene-4-aldehyde, and the ester-aldehydes of the formula

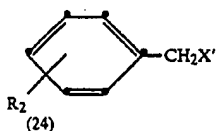
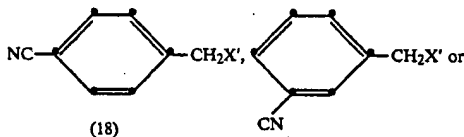
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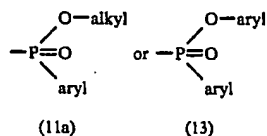
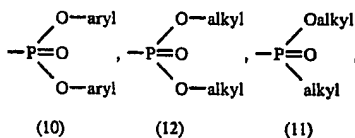
in which R_2 is a carboxylic acid ester group, especially a carboxylic acid ester group of the formula $-\text{COOY}$, in which Y is alkyl, halogenoalkyl, aralkyl, carbalkoxyalkyl, cyanoalkyl, hydroxyalkyl, aminoalkyl, alkylaminoalkyl or dialkylaminoalkyl, and all of the abovementioned alkyl groups and alkyl moieties in composite groups have 1 to 6 carbon atoms in each case; or Y is alkenyl having 3 to 6 carbon atoms, cycloalkyl having 5 to 6 carbon atoms, propargyl, tetrahydrofurfuryl or a group of the formula



in which X is hydrogen or methyl and n is an integer between 1 and 4 and the alkyl group has 1 to 6 carbon atoms, and to a process for their preparation. This process comprises reacting terephthalaldehyde with a compound of the formula

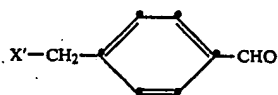


in which X' is a radical of the formula



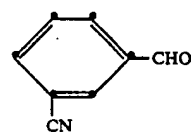
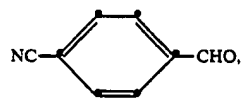
and separating off the corresponding aldehyde from the resulting mixture, by recrystallisation, which is repeated several times if necessary, or by chromatography.

Alternatively, it is also possible to react a compound of the formula

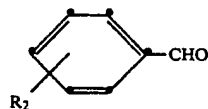


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in which X' is as defined above, with an aldehyde of the formula



or



The process conditions for the reaction of terephthalaldehyde with the compounds of the formulae (18), (19) and (24) correspond to those which have been indicated for the first stage of the process according to the invention for the preparation of the brightener mixtures. The final purification of the aldehydes is advantageously effected by chromatography, for example column chromatography, or preferably by recrystallisation, if necessary by repeated recrystallisation, if necessary with the addition of active charcoal or bleaching earth. Dioxane is the preferred solvent for the recrystallisation.

Preferred novel ester-aldehydes of the formula (23) are those in which R_2 is a group of the formula $-\text{COOY}_1$, in which Y_1 is alkyl having 1 to 4 carbon atoms.

The fluorescent brighteners according to the invention are used for the fluorescent brightening of a wide variety of synthetic, regenerated man-made or natural organic materials.

Without any restriction being implied by the following classification, examples of organic materials which can undergo fluorescent brightening are:

I. Synthetic organic materials of high molecular weight:

(a) Polymerisation products based on organic compounds containing at least one polymerisable carbon-carbon double bond, i.e. their homopolymers or copolymers as well as their after-treatment products, for example crosslinking, grafting or degradation products, polymer blends, or products obtained by modification of reactive groups, for example polymers based on α,β -unsaturated carboxylic acids or derivatives of such carboxylic acids, especially on acrylic compounds (for example acrylates, acrylic acid, acrylonitrile, acrylamides and their derivatives or their methacrylic analogues), on olefin hydrocarbons (for example ethylene, propylene, styrenes or dienes and also ABS polymers) and polymers based on vinyl and vinylidene compounds (for example vinyl chloride, vinyl alcohol and vinylidene chloride),

(b) Polymerisation products which can be obtained by ring opening, for example polyamides of the polycaprolactam type, and also polymers which are obtainable either by polyaddition or by polycondensation, such as polyethers or polyacetals,

(c) Polycondensation products or precondensates based on bifunctional or polyfunctional compounds with condensable groups, the homocondensation and co-condensation products, and after-treatment products thereof, for example polyesters, in particular saturated polyesters (for example polyesters of ethylene glycol/terephthalic acid) or unsaturated polyesters (for example maleic acid/dialcohol polycondensates and their crosslinking products with copolymerisable vinyl monomers), unbranched and branched polyesters (also including those based on polyhydric alcohols, for example alkyd resins), polyamides (for example hexamethylenediamine adipate), maleic resins, melamine resins, the precondensates and analogues thereof, polycarbonates and silicones,

(d) Polyaddition products, such as polyurethanes (crosslinked and uncrosslinked) and epoxide resins.

II. Regenerated man-made organic materials, for example cellulose esters of varying degrees of esterification (so-called 2½-acetate or triacetate) or cellulose ethers, regenerated cellulose (viscose or cuprammonium cellulose), or their after-treatment products, and casein plastics.

III. Natural organic materials of animal or vegetable origin, for example based on cellulose or proteins, such as cotton, wool, linen, silk, varnish gums, starch and casein.

The organic materials which are to undergo fluorescent brightening can be in the most diverse states of processing (raw materials, semi-finished goods or finished goods). On the other hand, they can be in the form of structures of the most diverse shapes, for example predominantly three-dimensionally expanded structures, such as sheets, profiles, injection mouldings, various machined articles, chips, granules or foams, and also predominantly two-dimensional structures, such as films, foils, lacquers, coverings, impregnations and coatings, or predominantly one-dimensional bodies, such as filaments, fibres, flocks and wires. The said materials can, on the other hand, also be in an unshaped state, in the most diverse homogeneous or inhomogeneous forms of division, as for example in the form of powders, solutions, emulsions, dispersions, latices, pastes or waxes.

Fibre materials can be, for example, in the form of endless filaments (stretched or unstretched), staple fibres, flocks, hanks, textile filaments, yarns, threads, non-wovens, felts, waddings, flocked structures or woven textile or bonded textile fabrics, knitted fabrics and papers, cardboards or paper pulps.

The fluorescent brighteners to be used according to the invention are of importance, in particular, for the treatment of organic textile materials, especially woven textile fabrics. If fibres, which can be in the form of staple fibres or endless filaments or in the form of hanks, woven fabrics, knitted fabrics, non-wovens, flocked substrates or bonded fabrics, are to be subjected to fluorescent brightening according to the invention, this is advantageously effected in an aqueous medium in which the particular compounds are present in a finely divided form (suspensions, so-called microdispersions, or, if desired, solutions). If desired, dispersing agents, stabilisers, wetting agents and further assistants can be added during the treatment.

The compounds can be applied in a neutral, alkaline or acid bath. The treatment is usually carried out at temperatures of about 20° to 140° C., for example at the boiling point of the bath or near it (about 90° C.). Solu-

tions or emulsions in organic solvents can also be used for the finishing, according to the invention, of textile substrates, as is practised in the dyeing industry in so-called solvent dyeing (pad-thermofixation, or exhaust dyeing processes in dyeing machines).

The fluorescent brightening agents of the present invention can further be added to or incorporated in the materials before or during their shaping. Thus, for example, they can be added to the compression moulding composition or injection moulding composition during the production of films, sheets (for example incorporated in polyvinyl chloride in a roll mill at elevated temperature) or mouldings.

If the shaping of man-made synthetic or regenerated man-made organic materials is effected by spinning processes or from spinning solutions/melts, the fluorescent brightening agents can be applied by the following processes:

addition to the starting substances (for example monomers) or intermediates (for example precondensates or prepolymers), i.e. before or during the polymerisation, polycondensation or polyaddition, sprinkling in powder form on polymer chips or granules for spinning solutions/melts, bath dyeing of polymer chips or granules for spinning solutions/melts, metered addition to spinning melts or spinning solutions and application to the spun tow before stretching.

The fluorescent brightening agents of the present invention can, for example, also be employed in the following use forms:

(a) in mixtures with dyestuffs (shading) or pigments (coloured pigments or especially, for example, white pigments); or as an additive to dyebaths, printing pastes, discharge pastes or reserve pastes, or for the after-treatment of dyeings, prints or discharge prints,

(b) in mixtures with carriers, wetting agents, plasticisers, swelling agents, antioxidants, light stabilisers, heat stabilisers and chemical bleaching agents (chlorite bleach or bleaching bath additives),

(c) in admixture with crosslinking agents or finishing agents (for example starch or synthetic finishes), and in combination with a wide variety of textile finishing processes, especially synthetic resin finishes (for example creaseproof finishes such as "wash-and-wear", "permanent-press" or "non-iron"), as well as flameproof finishes, soft-handle finishes, anti-soiling finishes or anti-static finishes, or antimicrobial finishes,

(d) incorporation of the fluorescent brightening agents into polymeric carriers (polymerisation, polycondensation or polyaddition products) in dissolved or dispersed form, for use, for example, in coating agents, impregnating agents or binders (solutions, dispersions and emulsions) for textiles, non-wovens, paper and leather,

(e) as additives to a wide variety of industrial products in order to render these more marketable (for example improving the appearance of soaps, detergents and pigments),

(f) in spinning bath preparations, i.e. as additives to spinning baths which are used for improving the slip for the further processing of synthetic fibres, or from a special bath prior to stretching the fibre,

(g) in agents for the fluorescent brightening of high molecular weight organic materials of the compositions indicated above, which agents can contain conventional

formulating additives and/or, if desired, further fluorescent brighteners from other categories of brighteners,

(h) as scintillators for various purposes of a photographic nature, for example for electrophotographic reproduction and supersensitising, and

(i) depending on the substitution, as laser dyes.

Agents of this type, which contain the fluorescent brighteners according to the invention, are likewise a subject of the invention.

Conventional formulating additives are, for example, very diverse assistants and extenders, for example anhydrous sodium sulfate, sodium sulfate decahydrate, sodium chloride, sodium carbonate, alkali metal phosphates, such as sodium orthophosphate or potassium orthophosphate, sodium pyrophosphate or potassium pyrophosphate and sodium tripolyphosphate or potassium tripolyphosphate, or alkali metal silicates. However, the agents according to the invention also include aqueous formulations, for example also the application solutions with which textile fibres are subjected to fluorescent brightening and which contain the conventional additives.

Within the scope of the agents according to the invention, particularly preferred agents are those which, in addition to a fluorescent brightener according to the invention (for example mixtures of the compounds (1) and (2), (3) and (4) or (3) and (6)) which gives rise to a greenish to bluish shade on the substrate to be treated, additionally also contain a fluorescent brightener which gives rise to a reddish shade on the substrate to be treated.

Such combinations have the advantage that a particularly attractive neutral white shade of high brilliance can be achieved by this means on textile fibres, in particular on polyester fibres.

Highly advantageous agents are, therefore, those which contain a fluorescent brightener consisting of the compounds (3) and (4) or (3) and (6), or of other mixtures of a symmetrical and unsymmetrical component which are constituents of the fluorescent brighteners according to the invention, and, in addition, a fluorescent brightener from the category of the naphthalimides, bis-benzoxazolyl-ethylenes, bis-benzoxazolyl-thiophenes, stilbenylbenzoxazoles, naphthotriazol-2-ylstilbenes (disclosed in German Offenlegungsschriften Nos. 2,539,537 and 2,539,461) or the coumarins, for example the 3-phenyl-7-pyrazolylcoumarins, the 3-pyrazolyl-7-v-triazolylcoumarins or the 3-v-triazolylcoumarins (disclosed in Swiss Patent Specification Nos. 566,359 and 592,189), and in particular those which contain, as the fluorescent brightener active substance, 5-90% and in particular 30-70% of a fluorescent brightener according to the invention (for example mixtures of the compounds (1) and (2), (3) and (4) or (3) and (6)) which give rise to a greenish to bluish shade on the substrate treated and 95-10%, and in particular 70-30%, of a fluorescent brightener which gives rise to a reddish shade on the substrate treated, the latter brightener preferably being a brightener from the abovementioned categories.

Brighteners from the category of the naphthotriazol-ylstilbenes and of the triazolylcoumarins are particularly suitable in agents according to the invention as fluorescent brighteners which give rise to a reddish shade.

Examples of fluorescent brighteners which give rise to a reddish shade and which can be employed in agents according to the invention are, inter alia: 2,5-bis(ben-

zoxazol-2-yl)-thiophen, 4-(5-methylbenzoxazol-2-yl)-4'-carbomethoxystilbene, 1-methyl-5-methoxynaphthalimide, 3-phenyl-7-(4-phenyl-5-methyl-v-triazol-2-yl)-coumarin, 3-(4-chloropyrazol-1-yl)-7-(4-phenyl-5-methyl-v-triazol-2-yl)-coumarin and, in particular, 3-(2-phenyl-v-triazol-4-yl)-7-methoxycoumarin and 4-(naphtho[1,2-d]triazol-2-yl)-4'-carbomethoxystilbene.

Substrates which are particularly preferentially brightened using the fluorescent brighteners according to the invention are those made of polyester, especially textile materials made of polyester.

If the brightening process is combined with textile treatment or finishing methods, the combined treatment can in many cases advantageously be carried out with the aid of appropriate stable preparations which contain the fluorescent brightener compounds in such a concentration that the desired white effect is achieved.

In certain cases, the fluorescent brighteners are made fully effective by an after-treatment. This can be, for example, a chemical treatment (for example acid treatment), a heat treatment or a combined chemical/heat treatment. Thus, for example, the appropriate procedure to follow in brightening a number of fibre substrates, for example polyester fibres, with the fluorescent brightening agents of the present invention, is to impregnate these fibres with the aqueous dispersions (or, if desired, also solutions) of the fluorescent brightening agents at temperatures below 75° C., for example at room temperature, and to subject them to a dry heat treatment at temperatures above 100° C., it generally being advisable additionally to dry the fibrous material beforehand at a moderately elevated temperature, for example at not less than 60° C. to about 130° C. The heat treatment in the dry state is then advantageously carried out at temperatures between 120° and 225° C., for example by heating in a drying chamber, by ironing within the specified temperature range or by treatment with dry, superheated steam. Drying and the dry heat treatment can also be carried out in immediate succession or combined in a single operation.

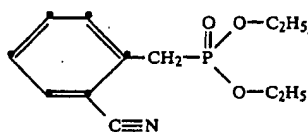
The amount of the fluorescent brightening agents to be used according to the invention, based on the material to be subjected to fluorescent brightening, can vary within wide limits. A marked and lasting effect can be obtained even with very small amounts, in certain cases, for example, amounts of 0.001 percent by weight. However, it is also possible to use amounts of up to about 0.8 percent by weight and, if necessary, of up to about 2 percent by weight. For most practical purposes, it is preferable to use amounts of between 0.01 and 0.5 percent by weight.

In the examples which follow parts are by weight, unless indicated otherwise, and percentages are by weight.

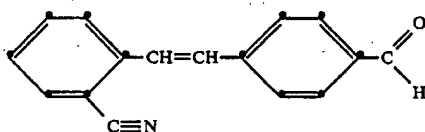
EXAMPLE 1

53.6 g of terephthalaldehyde are suspended in 300 ml of absolute ethanol and 144 g of a 30% methanolic solution of sodium methylate are added in the course of 15 minutes at 20° to 25° C., with stirring and under nitrogen. A virtually clear solution forms, and 102 g of the phosphonate of the formula

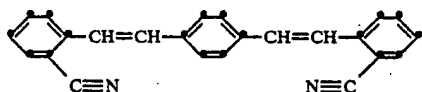
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are added to this solution in the course of 20 minutes at 20° to 25° C., with stirring and under nitrogen, and the reaction product immediately precipitates as crystals. The resulting thick crystalline reaction slurry is now stirred for a further six hours at 20° to 25° C. under nitrogen and is then filtered with suction and the crystalline material is washed with approximately 50 ml of absolute ethanol and dried in vacuo at 50° C. to constant weight. 60.06 g (approximately 64.4% of theory) of a pale yellow crystalline powder with a melting point of 144° to 149° C. are obtained, and this can be identified by analysis by gas chromatography as a mixture consisting of 87.8% of the compound of the formula



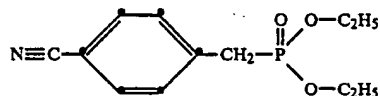
and 11.3% of the compound of the formula



The phosphonate of the formula (14) which is used as the starting material is prepared analogously to Example 1 of German Offenlegungsschrift No. 1,921,466 and purified by distillation (boiling point_{0.35}: 136°-138° C.).

23.3 g of a mixture of compounds (16) and (4), which has been obtained as described above, and 25.3 g of the

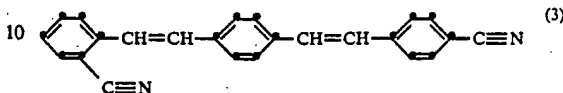
phosphonate of the formula



are suspended in 200 ml of dimethylformamide, and 19.0 g of a 30% methanolic solution of sodium methylate are added in the course of 30 minutes at 30° C., with stirring and under nitrogen, the reaction temperature rising to 40° C. A virtually clear solution first forms and towards the end of the addition of the sodium methylate solution the reaction product precipitates out from this solution as a thick crystalline slurry. The reaction mixture is now stirred for a further four hours at 30° C. under nitrogen and is then diluted at 20° C. with 200 ml of water and neutralised with about 1 ml of glacial acetic acid. The reaction product is filtered off with suction, washed with about 100 ml of dimethylformamide/water (1:1)

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and then with about 100 ml of methanol and dried in vacuo at 100° C. to constant weight. 28.9 g (approximately 86.9% of theory) of a pale yellow crystalline powder with a melting point of 188° to 233° C. are obtained and on analysis by gas chromatography this proves to be a mixture consisting of 91.2% of the compound of the formula

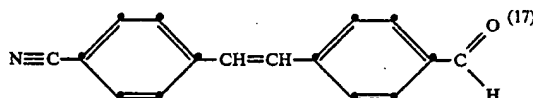


and 7.7% of the compound of the formula (4).

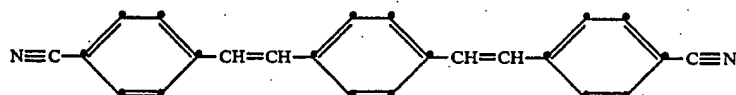
The phosphonate of the formula (15) which is used as starting material is prepared in accordance with Example 1 of German Offenlegungsschrift No. 1,921,466.

EXAMPLE 2

67 g of terephthalaldehyde are suspended in 300 ml of absolute methanol and 180 g of a 30% methanolic solution of sodium methylate are added in the course of 15 minutes at 20° to 25° C., with stirring and under nitrogen. A virtually clear solution forms, and a solution of 126.6 g of the phosphonate of the formula (15) in 100 ml of absolute methanol is added in the course of 20 minutes at 20° to 25° C., with stirring and under nitrogen, and the reaction product immediately precipitates out as crystals. The resulting crystalline reaction mixture is further treated as described in Example 1. 106.1 g (approximately 91.0% of theory) of a pale yellow crystalline powder with a melting point of 198° to 205° C. are obtained, and on analysis this proves to be a mixture consisting of 92.3% of the compound of the formula



and 7.1% of the compound of the formula



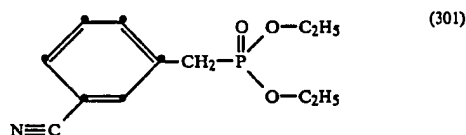
After recrystallising three times from dioxane, and with the aid of active charcoal, 40.6 g of the aldehyde of the formula (17) are obtained in the form of long pale yellow needles with a melting point of 207° to 210° C. 23.3 g of a mixture of the compounds (17) and (6), which has been obtained as described above, and 25.3 g of the phosphonate of the formula (14) are suspended in 200 ml of dimethylformamide, and 19 g of a 30% methanolic solution of sodium methylate are added in the course of 20 minutes at 30° C., with stirring and under nitrogen, the reaction temperature rising to 40° C. A virtually clear solution first forms and towards the end of the addition of the sodium methylate solution the reaction product precipitates out from this solution in the form of a thick crystalline slurry. The reaction mixture is further treated as described in Example 1. 30.56 g (approximately 91.9% of theory) of a pale yellow crystalline powder with a melting point of 200° to 230°

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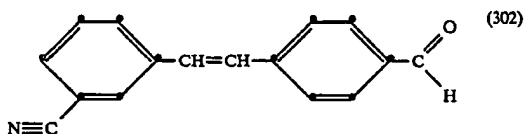
C. are obtained and on analysis this proves to be a mixture consisting of 95.7% of the compound of the formula (3) and 3.2% of the compound of the formula (6).

EXAMPLE 3

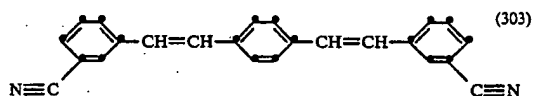
26.8 g of terephthalaldehyde are suspended in 100 ml of absolute methanol, and 72 g of a 30% methanolic solution of sodium methylate are added in the course of 15 minutes at 20° to 25° C., with stirring and under nitrogen. A virtually clear solution forms, and a solution of 50.6 g of the phosphonate of the formula



in 60 ml of absolute methanol is added in the course of 20 minutes at 20° and 25° C., with stirring and under nitrogen, and the reaction product slowly precipitates out as crystals. The resulting crystalline reaction mixture is now stirred for a further 24 hours at 20° to 25° under nitrogen, cooled to 0° C. and then filtered with suction, and the crystalline material is washed with about 50 ml of absolute ethanol and dried in vacuo at 50° C. to constant weight. 32.0 g (approximately 68.7% of theory) of a pale yellow crystalline powder with a melting point of 117° to 192° C. are obtained, and on analysis this proves to be a mixture consisting of 81.5% of the compound of the formula



and 17.2% of the compound of the formula



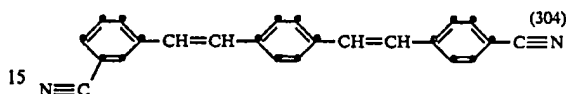
After recrystallising twice from alcohol, and with the removal of the compound of the formula (303) which is insoluble in alcohol, 14.5 g of the aldehyde of the formula (302) are obtained in the form of pale yellow needles with a melting point of 117° to 119° C.

The phosphonate of the formula (301), which is used as starting material, is prepared in accordance with Example 2 of British Patent Specification No. 920,988.

23.3 g of a mixture of the compounds (302) and (303), which has been obtained as described above, and 25.3 g of the phosphonate of the formula (15) are suspended in 200 ml of dimethylformamide, and 19 g of a 30% methanolic solution of sodium methylate are added in the course of 15 minutes at 30° C., with stirring and under nitrogen. A virtually clear solution first forms and towards the end of the addition of the sodium methylate solution the reaction product precipitates out from this solution in the form of a thick crystalline slurry, the reaction temperature rising to 40° C. The reaction mixture is now stirred for a further four hours at 30° C. under nitrogen and is then diluted at 0° C. with 200 ml of water and neutralised with about 1 ml of glacial

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acetic acid. The reaction product is filtered off with suction, washed with about 100 ml of dimethylformamide/water (1:1) and then with about 80 ml of ethanol and dried in vacuo at 100° C. to constant weight. 28.55 g (approximately 85.9% of theory) of a pale yellow crystalline powder with a melting point of 199° to 217° C. are obtained, and on analysis this proves to be a mixture consisting of 88.3% of the compound of the formula



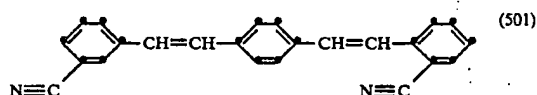
and 10.9% of the compound of the formula (303).

EXAMPLE 4

23.3 g of the mixture of the compounds (17) and (6), which has been obtained according to Example 2, and 25.3 g of the phosphonate of the formula (301) are reacted as described in Example 3. 29.4 g (approximately 88.5% of theory) of a pale yellow crystalline powder with a melting point of 204° to 220° C. are obtained and on analysis this proves to be a mixture consisting of 95.7% of the compound of the formula (304) and 3.8% of the compound of the formula (6).

EXAMPLE 5

23.3 g of the mixture of the compounds (302) and (303) which has been obtained according to Example 3 and 25.3 g of the phosphonate of the formula (14) are reacted in 100 ml of dimethylformamide as described in Example 3. 23.5 g (approximately 70% of theory) of a pale yellow crystalline powder with a melting point of 174° to 183° C. are obtained, and on analysis this proves to be a mixture consisting of 85.1% of the compound of the formula



and 13.8% of the compound of the formula (303).

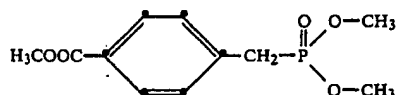
EXAMPLE 6

23.3 g of the mixture of the compounds (16) and (4), which has been obtained according to Example 1, and 25.3 g of the phosphonate of the formula (301) are reacted in 100 ml of dimethylformamide as described in Example 3. 24.5 g (approximately 73.5% of theory) of a pale yellow crystalline powder with a melting point of 176° to 188° C. are obtained, and on analysis this proves to be a mixture consisting of 91.6% of the compound of the formula (501) and 7.1% of the compound of the formula (4).

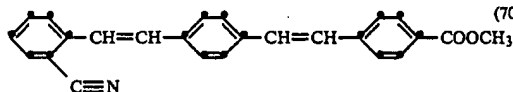
EXAMPLE 7

7 g of the mixture of the compounds (16) and (4), which has been obtained according to Example 1, and 7.8 g of the phosphonate of the formula

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are reacted in 80 ml of dimethylformamide as described in Example 3. 9.5 g (approximately 87% of theory) of a yellow crystalline product with a melting point of 187° to 205° C. are obtained, and on analysis this proves to be a mixture consisting of 93.3% of the compound of the formula

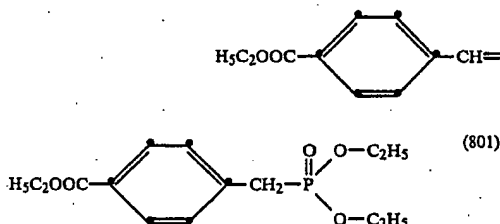


and 5.6% of the compound of the formula (4).

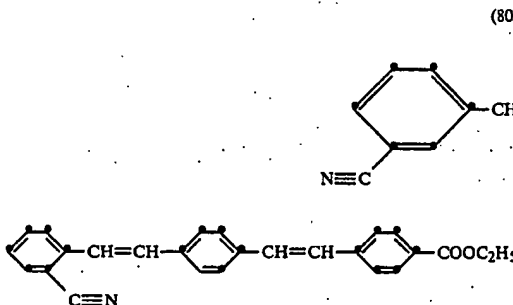
The phosphonate of the formula (701), which is used as starting material, is prepared in accordance with Example 2 of British Patent Specification No. 929,436.

EXAMPLE 8

9.3 g of the mixture of the compounds (16) and (4), which has been obtained according to Example 1, and 12 g of the phosphonate of the formula



are suspended in 120 ml of dimethylformamide, and 22 ml of an ethanolic 2M solution of sodium ethylate are added in the course of 15 minutes at 30° C., with stirring and under nitrogen. The reaction mixture is worked up as described in Example 3. 13 g (approximately 86% of theory) of a yellow crystalline product with a melting point of 178° to 181° C. are obtained, and on analysis this proves to be a mixture consisting of 95.3% of the compound of the formula



and 3.9% of the compound of the formula (4).

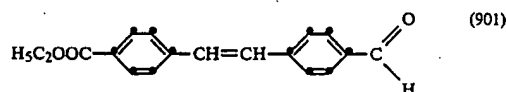
The phosphonate of the formula (801), which is used as starting material, is prepared analogously to Example

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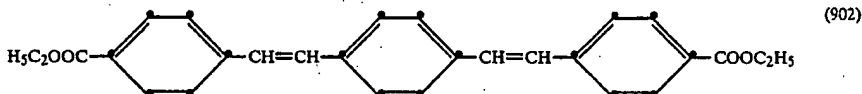
2 of British Patent Specification No. 929,436 and purified by distillation (boiling point_{0.25}: 181°-185° C.).

EXAMPLE 9

40 g of terephthalaldehyde are suspended in 100 ml of absolute ethanol, and 300 ml of an ethanolic 2M solution of sodium ethylate are added in the course of 15 minutes at 20° to 25° C., with stirring and under nitrogen. A virtually clear solution forms, and 90 g of the phosphonate of the formula (801) are added in the course of 20 minutes at 20° to 25° C., with stirring and under nitrogen, and the reaction product precipitates immediately as crystals. The resulting thick crystalline reaction slurry is now stirred for a further 16 hours at room temperature under nitrogen and is then filtered with suction, and the crystalline product is washed with 50 ml of absolute ethanol and dried in vacuo at 50° C. to constant weight. 64 g (approximately 76% of theory) of a pale yellow crystalline powder with a melting point of 102° to 169° C. are obtained, and this can be identified by analysis as a mixture consisting of 89.5% of the compound of the formula



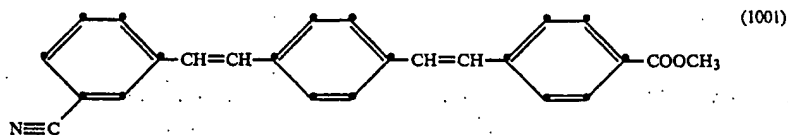
and 9.1% of the compound of the formula



After recrystallising twice from ethanol, and with removal of the compound of the formula (902) which is insoluble in ethanol, 32 g of the aldehyde of the formula (901) are obtained in the form of long, pale yellow needles with a melting point of 103° to 105° C.

EXAMPLE 10

8 g of the mixture of the compounds (302) and (303), which has been obtained according to Example 3, and 9 g of the phosphonate of the formula (701) are reacted in 80 ml of dimethylformamide as described in Example 3. 10 g (approximately 78% of theory) of a pale yellow crystalline powder with a melting point of 228° to 236° C. are obtained, and on analysis this proves to be a mixture consisting of 93.4% of the compound of the formula



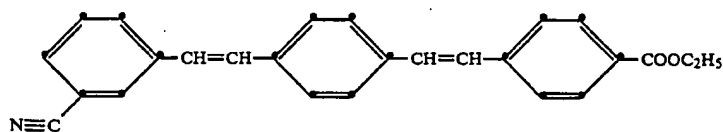
and 5.5% of the compound of the formula (303).

EXAMPLE 11

9.3 g of the mixture of the compounds (302) and (303), which has been obtained according to Example 3, and 12 g of the phosphonate of the formula (801) are suspended in 120 ml of dimethylformamide, and 22 ml of an ethanolic 2M solution of sodium ethylate are added

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in the course of 15 minutes at 30° C., with stirring and under nitrogen. The reaction mixture is worked up as described in Example 3. 12.5 g (approximately 82% of theory) of a yellow crystalline product with a melting point of 194° to 197° C. are obtained, and on analysis this proves to be a mixture consisting of 92.6% of the compound of the formula



and 6.5% of the compound of the formula (303).

EXAMPLE 12

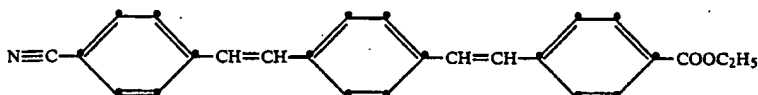
11.7 g of the mixture of the compounds (17) and (6), which has been obtained according to Example 2, and 13 g of the phosphonate of the formula (701) are reacted in 100 ml of dimethylformamide as described in Example 3. 16 g (approximately 87% of theory) of a yellow crystalline powder with a melting point of 219° to 225° C. are obtained, and on analysis this proves to be a mixture consisting of 97.2% of the compound of the formula



and 2.6% of the compound of the formula (6).

EXAMPLE 13

9.3 g of the mixture of the compounds (17) and (6), which has been obtained according to Example 2, and 12 g of the phosphonate of the formula (801) are suspended in 120 ml of dimethylformamide, and 22 ml of an ethanolic 2M solution of sodium ethylate are added in the course of 15 minutes at 30° C., with stirring and under nitrogen. The reaction mixture is worked up as described in Example 3. 13.5 g (approximately 89% of theory) of a yellow crystalline powder with a melting point of 219° to 221° C. are obtained, and on analysis this proves to be a mixture consisting of 95.5% of the compound of the formula

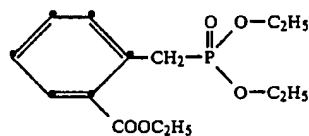


and 3.4% of the compound of the formula (6).

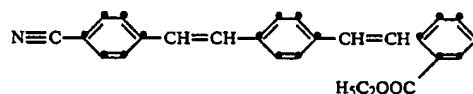
EXAMPLE 14

18.6 g of the mixture of the compounds (17) and (6), which has been obtained according to Example 2, and 24 g of the phosphonate of the formula

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are suspended in 60 ml of dimethylformamide, and 35 ml of an ethanolic 2.5M solution of sodium ethylate are added in the course of 15 minutes at 30° C., with stirring and under nitrogen. The reaction mixture is worked up as described in Example 3. 11.5 g (approximately 38% of theory) of a yellow crystalline powder with a melting point of 143° to 169° C. are obtained, and on analysis this proves to be a mixture consisting of 90.6% of the compound of the formula

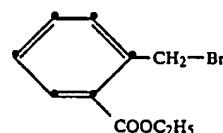


and 8.3% of the compound of the formula (6).

The phosphonate of the formula (1401), which is used as starting material, is prepared as follows:

55.2 g of sodium are initially introduced into 360 ml of toluene, and the toluene is heated to the reflux temperature. The molten sodium is finely powdered with the aid of a vibro mixer, with rapid cooling. First 5 ml of anhydrous ethanol and then 331 g of diethyl phosphite are now added dropwise in the course of one hour to the resulting suspension of sodium in toluene, at 60° C. and with vigorous mixing using the vibro mixer, and

the sodium rapidly goes into solution. After a further hour at 60° C., the sodium has dissolved completely and a clear solution forms. 600 g of the compound of the formula

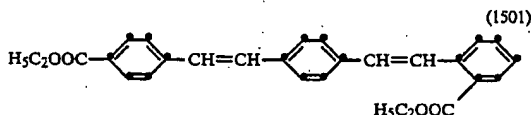


are now added dropwise in the course of one hour to this solution of the sodium salt of the diethyl phosphite, at 60° C. with mixing with the vibro mixer, and sodium bromide precipitates out. The resulting suspension is mixed for 20 hours at 60° C. using the vibro mixer and is then cooled to room temperature, taken up in methylene chloride, washed with a 2N sodium carbonate solution and then with water until neutral, dried over sodium sulphate and concentrated to dryness in vacuo in a rotary evaporator. 696 g of a yellow-brown oil are obtained and after distillation this gives 503 g (70% of theory) of the phosphonate of the formula (1401) in the form of a yellow oil (boiling point_{0.08}: 158°-160° C.).

The ethyl 2-bromomethyl-benzoate of the formula (1403) is prepared in accordance with J. Chem. Soc. 121, 2202-2215 (1922).

EXAMPLE 15

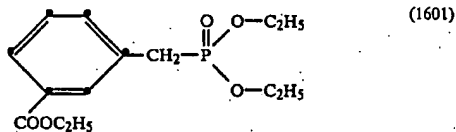
19.6 g of the mixture of the compounds (901) and (902), which has been obtained according to Example 9, and 21 g of the phosphonate of the formula (1401) are suspended in 60 ml of dimethylformamide, and 31 ml of an ethanolic 2.5M solution of sodium ethylate are added in the course of 15 minutes at 30° C., with stirring and under nitrogen. The reaction mixture is worked up as described in Example 3. 11 g (approximately 37% of theory) of a pale yellow crystalline powder with a melting point of 125° to 250° C. is obtained, and on analysis this proves to be a mixture consisting of 87.5% of the compound of the formula



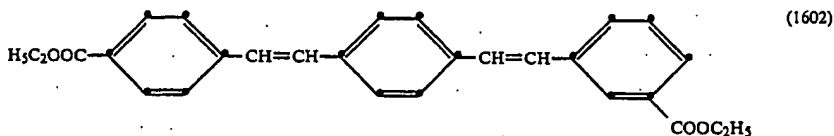
and 12.1% of the compound of the formula (902).

EXAMPLE 16

19.6 g of the mixture of the compounds (901) and (902), which has been obtained according to Example 9, and 21 g of the phosphonate of the formula



are suspended in 50 ml of dimethylformamide, and 31 ml of an ethanolic 2.5M solution of sodium ethylate are added in the course of 15 minutes at 30° C., with stirring and under nitrogen. The reaction mixture is worked up as described in Example 3. 23 g (approximately 74% of theory) of a pale yellow crystalline powder with a melting point of 183° to 250° C. are obtained, and on analysis this proves to be a mixture consisting of 94.7% of the compound of the formula



and 5.4% of the compound of the formula (902).

The phosphonate of the formula (1601), which is used as starting material, is prepared analogously to Example 2 of British Patent Specification No. 929,436 and purified by distillation (boiling point_{0.3}: 183°-185° C.).

EXAMPLE 17

1 g of the fluorescent brightener consisting of 91.2% of the compound of the formula (3) and 7.7% of the compound of the formula (4) is dispersed in 1,000 ml of water. 100 ml of water containing 0.1 g of a fatty alcohol polyglycol ether are added to 7.5 ml of this dispersion. Polyester fabric weighing 15 g is put into this brightener dispersion, which has been warmed to 60° C. The temperature is raised to 120° C. in the course of 15 to 20 minutes, and this temperature is maintained for 30 minutes. The dispersion is then cooled to 60° C. in the course of 10 to 15 minutes. The fabric is then rinsed for 2 minutes in running cold water and is then dried for 20 minutes at 60° C.

The fabric treated in this way has a powerful white effect of good fastness to light.

Similarly good white effects are obtained when this procedure is repeated using a fluorescent brightener consisting of 95.7% of the compound of the formula (3) and 3.2% of the compound of the formula (6) or a fluorescent brightener consisting of 88.3% of the compound of the formula (304) and 10.9% of the compound of the formula (303) in place of the fluorescent brightener mentioned.

EXAMPLE 18

Polyester fabric is padded at room temperature with an aqueous dispersion which contains, per liter, 0.5 g of a fluorescent brightening agent consisting of 91.2% of the compound of the formula (3) and 7.7% of the compound of the formula (4) and also 1 g of an adduct of about 8 mols of ethylene oxide and 1 mol of p-tert-octylphenol. The liquor pick-up is 60 to 70%. The fabric is dried at 100° C. and is then heated to 180° C. for 15 seconds.

The fabric treated in this way has a powerful white effect of good fastness to light.

Similarly good white effects are obtained when this procedure is repeated using a fluorescent brightening agent consisting of 95.7% of the compound of the formula (3) and 3.2% of the compound of the formula (6) or a fluorescent brightening agent consisting of 88.3% of the compound of the formula (304) and 10.9% of the compound of the formula (303) in place of the fluorescent brightening agent mentioned.

Similar white effects are achieved by the two procedures of Examples 17 and 18 when the fluorescent brightening agent used is a two-component fluorescent brightener consisting of 95.7% of the compound of the formula (304) and 3.8% of the compound of the formula (6); 85.1% of the compound of the formula (303); 91.6% of the compound of the formula (301) and 7.1% of the compound of the formula (4); 93.3% of the compound

of the formula (702) and 5.6% of the compound of the formula (4); 95.3% of the compound of the formula (802) and 3.9% of the compound of the formula (4); 93.4% of the compound of the formula (1001) and 5.5% of the compound of the formula (303); 92.6% of the compound of the formula (1101) and 6.5% of the compound of the formula (303); 97.2% of the compound of the formula (1201) and 2.6% of the compound of the formula (6); 95.5% of the compound of the formula (1301) and 3.4% of the compound of the formula (6); 90.6% of the compound of the formula (1402) and 8.3% of the compound of the formula (6); 87.5% of the compound of the formula (1501) and 12.1% of the compound of the formula (902); or 94.7% of the compound of the formula (1602) and 5.4% of the compound of the formula (902).

EXAMPLE 19

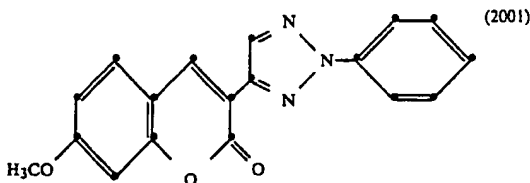
1 g of the fluorescent brightener consisting of 91.2% of the compound of the formula (3) and 7.7% of the compound of the formula (4) is dispersed in 1,000 ml of water. 100 ml of water containing 0.06 g of an alkylpolyglycol ether are added to 3 ml of this dispersion. Polyamide fabric (polyamide 6 or 66) weighing 3 g is put into this brightener dispersion, which has been warmed to 60° C. The temperature is raised to 95° to 97° C. in the course of 10 to 15 minutes and this temperature is maintained for 30 minutes. The fabric is then rinsed for 2 minutes in running cold water and is then dried for 20 minutes at 60° C.

The fabric obtained in this way has a powerful white effect of good fastness to light.

Similarly good white effects are obtained when this procedure is repeated using a fluorescent brightening agent consisting of 95.7% of the compound of the formula (3) and 3.2% of the compound of the formula (6) or a fluorescent brightening agent consisting of 88.3% of the compound of the formula (304) and 10.9% of the compound of the formula (303) in place of the fluorescent brightening agent mentioned.

EXAMPLE 20

A bath is prepared which contains, per liter of soft water, 0.0125, 0.025 or 0.05% by weight, based on the polyester material to be brightened, of a fluorescent brightener mixture consisting of a fluorescent brightener comprising 95.7% of the compound of the formula (3) and 3.2% of the compound of the formula (6) and a fluorescent brightener of the formula



in a mixing ratio of 1:2 or 2:1, and also 1 g of a fatty alcohol polyglycol ether.

Using a liquor ratio of 1:20, a polyester fabric ("Terylene Type 540") is put, at 40° C., into the bath, which is in a conventional HT dyeing apparatus. The bath is warmed to 110°, 120° or 130° C. in the course of 30 minutes and is kept at the particular temperature for 30 minutes. It is then cooled to 40° C. in the course of 15 minutes. The treated fabric is rinsed for 30 seconds in running, softened water and then dried.

The pieces of fabric treated have powerful, brilliant white effects with a pleasing shade. The greenish-bluish shade obtained when fluorescent brightening is carried out using the fluorescent brightener consisting of the compounds (3) and (6) on its own has been shifted distinctly into the more reddish range.

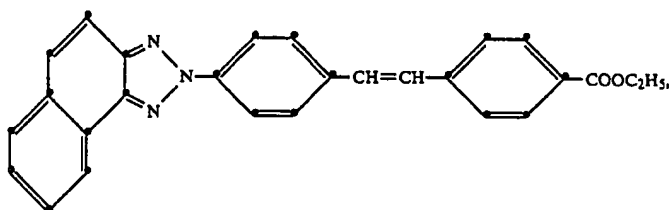
EXAMPLE 21

Polyester fabric ("Terylene Type 540") is padded at room temperature with an aqueous dispersion which contains, per liter, 0.125, 0.25, 0.5 or 1 g of a fluorescent brightener mixture consisting of a fluorescent brightener comprising 95.7% of the compound of the formula (3) and 3.2% of the compound of the formula (6) and a fluorescent brightener of the formula (2001) in a mixing ratio of 1:2, or 2:1, and also 1 ml of an alkylphenol polyglycol ether. The liquor pick-up is 80%. The fabric is dried at 80° C. for 10 minutes and is then thermofixed for 30 seconds at 180°, 220° or 220° C.

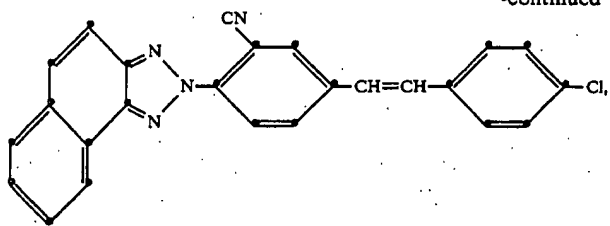
The pieces of fabric treated have powerful, brilliant white effects with a pleasing shade. The greenish-bluish shade obtained when fluorescent brightening is carried out using the fluorescent brightener consisting of the compounds (3) and (6) on its own has been shifted distinctly into the more reddish range.

EXAMPLE 22

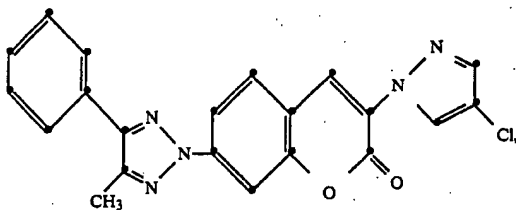
Example 20 or 21 is repeated, except that, in place of the fluorescent brightener of the formula (2001), the same amount of one of the fluorescent brighteners of the formulae



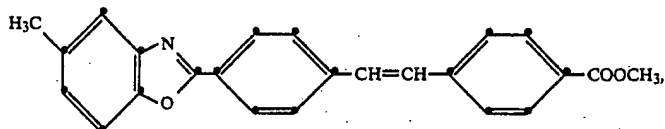
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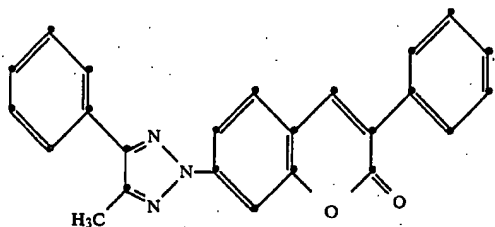
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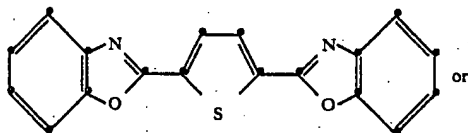
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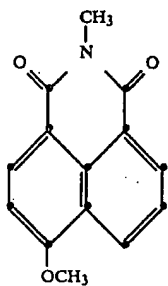
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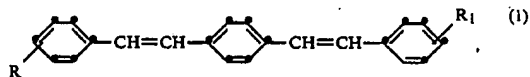
is employed. Good effects, similar to those described in Examples 20 and 21, are obtained on the pieces of fabric treated.

The fluorescent brightener consisting of the compounds (3) and (6) can also be replaced by any other desired two-component fluorescent brightening agent obtainable according to Examples 1, 3-8 and 10-16.

What is claimed is:

1. A fluorescent brightener, consisting of 51-99% of an unsymmetrically substituted compound of the formula

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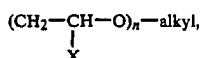
65 in which R and R₁ are identical or different and, if R and R₁ are identical, the substituent positions of R and R₁ must be different, and in which R and R₁ independently of one another are CN or a carboxylic acid ester

group, and 49-1% of a symmetrically substituted compound of the formula



in which R is as defined above and the two R's are bonded to identical positions in their phenyl rings.

2. A fluorescent brightener according to claim 1, wherein, in the two individual components, R and R₁ independently of one another are CN or a group of the formula —COOY, in which Y is alkyl, halogenoalkyl, aralkyl, carbalkoxyalkyl, cyanoalkyl, hydroxyalkyl, aminoalkyl, alkylaminoalkyl or dialkylaminoalkyl, and all of the abovementioned alkyl groups and alkyl moieties in composite groups in each case have 1 to 6 carbon atoms; or Y is alkenyl having 3 to 6 carbon atoms, cycloalkyl having 5 to 6 carbon atoms, propargyl, tetrahydrofurfuryl or a group of the formula

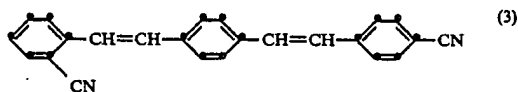


in which X is hydrogen or methyl and n is an integer between 1 and 4 and the alkyl group has 1 to 6 carbon atoms.

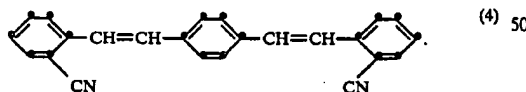
3. A fluorescent brightener according to claim 2, wherein R and R₁, in each case independently of one another, are —CN or —COOY, in which Y is alkyl having 1 to 4 C atoms.

4. A fluorescent brightener according to claim 2, wherein R and R₁ are CN.

5. A fluorescent brightener according to claim 4, consisting of 51-99% of the compound of the formula



and 49-1% of the compound of the formula

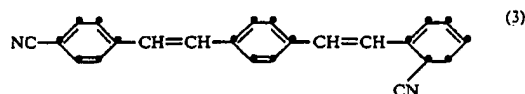


6. A fluorescent brightener of claim 5, consisting of 70-99% of the unsymmetrically substituted compound and 30 to 1% of the symmetrically substituted compound.

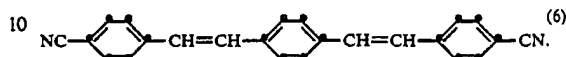
7. A fluorescent brightener of claim 5, consisting of 80-99% of the unsymmetrically substituted compound and 20-1% of the symmetrically substituted compound.

8. A fluorescent brightener of claim 5, consisting of 90-99% of the unsymmetrically substituted compound and 10 to 1% of the symmetrically substituted compound.

9. A fluorescent brightener according to claim 4, consisting of 51-99% of the compound of the formula



and 49-1% of the compound of the formula



10. A fluorescent brightener of claim 9, consisting of 70-99% of the unsymmetrically substituted compound and 30 to 1% of the symmetrically substituted compound.

11. A fluorescent brightener of claim 9, consisting of 80-99% of the unsymmetrically substituted compound and 30 to 1% of the symmetrically substituted compound.

12. A fluorescent brightener of claim 9, consisting of 80-99% of the unsymmetrically substituted compound and 30 to 1% of the symmetrically substituted compound.

13. A fluorescent brightener according to claim 1, consisting of 70-99% of the unsymmetrically substituted compound, and 30 to 1% of the symmetrically substituted compound.

14. A fluorescent brightener according to claim 13, consisting of 80-99% of the unsymmetrically substituted compound, and 20-1% of the symmetrically substituted compound.

15. A fluorescent brightener according to claim 14, consisting of 90-99% of the unsymmetrically substituted compound, and 10-1% of the symmetrically substituted compound.

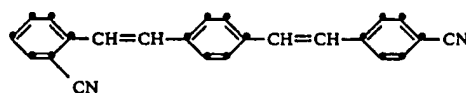
16. An agent for the fluorescent brightening of high molecular weight organic materials, which contains a fluorescent brightener defined in claim 1.

17. An agent according to claim 16, which, in addition to a fluorescent brightener, which gives rise to a greenish to bluish shade on the treated substrate, contains a fluorescent brightener which gives rise to a reddish shade on the treated substrate.

18. An agent according to claim 17, which contains, in addition, a fluorescent brightener from the category of the naphthalimides, bis-benzoxazolyl-ethylenes, bis-benzoxazolyl-thiophenes, stilbenyl-benzoxazoles, naphthotriazolyl-stilbenes or triazolylcoumarins.

19. An agent according to claim 18, which contains, as the fluorescent brightener active substance, 5-90% of a fluorescent brightener, which gives rise to a greenish to bluish shade on the treated substrate, and 95-10%, of a fluorescent brightener which gives rise to the reddish shade on the treated substrate.

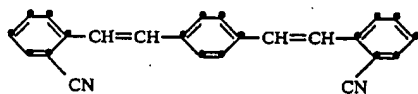
20. An agent according to claim 19, which contains a fluorescent brightener consisting of the compounds



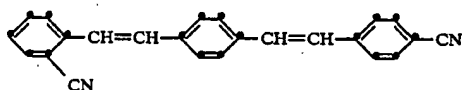
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or



and

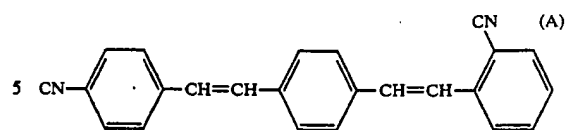


and, in addition, a fluorescent brightener from the category of the naphthotriazolyl-stilbenes or of the triazolylcoumarins.

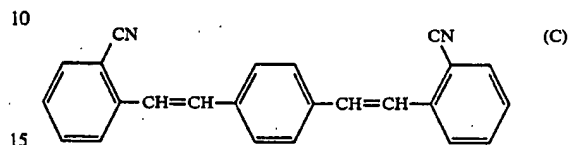
21. A fluorescent brightener according to claim 1 wherein R and R₁ must have different substituent positions in formula (1).

22. A mixture of optical brightener compounds consisting of a compound of formula (A)

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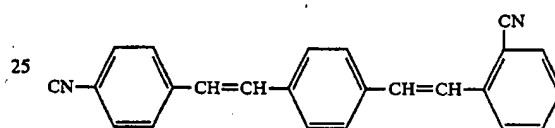


and a compound of formula (C) where formula (C) is

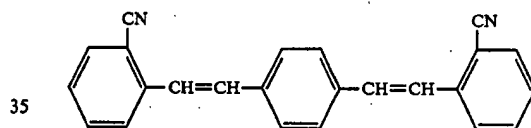


23. A mixture according to claim 1 of 51-99% of a compound of formula (A) and 48-1% of a compound of formula (C).

24. A mixture of optical brightener compounds consisting of 70% of a compound of the formula



and 30% of a compound of the formula



* * * * *

Disclaimer

4,778,623.—*Leonardo Guglielmetti*, Bottmingen, Switzerland. FLOURESCENT BRIGHTENERS CONSISTING OF BIS-STYRLBENZENE COMPOUNDS, A PROCESS FOR THEIR PREPARATION AND THEIR USE. Patent dated Oct. 18, 1988. Disclaimer filed Jun. 21, 1990, by the assignee, Ciba-Geigy Corporation.

Hereby enters this disclaimer to claims 16 through 20 of said patent.
[*Official Gazette August 14, 1990*]

(10) RELATED PROCEEDINGS APPENDIX

As the appellants are not aware of any other related proceedings, no copies of decisions rendered by a court or the board are attached.